

## STARCH ESTERIFICATION METHOD

## Field of the invention

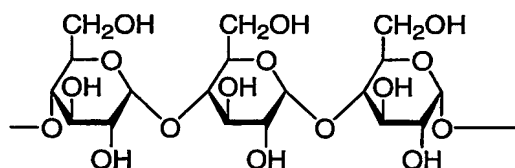
5 The present invention is directed to a new method for preparing organic starch esters.

## Background art

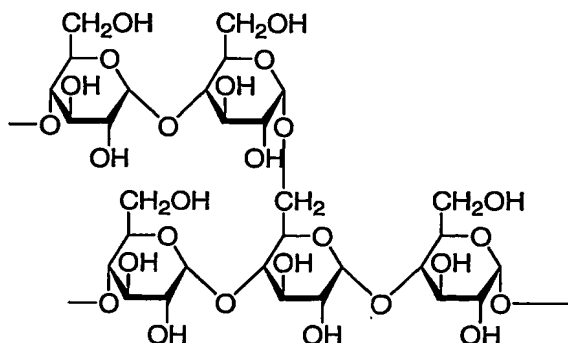
## Starch

10 Unlike other carbohydrates and edible polymers, starch occurs as discrete particles called starch granules. These are generally composed of two type of molecules, amylose and amylopectin. Of these, amylose is a linear (1,4)- $\alpha$ -D-glucan, while amylopectin is a branched, bushlike structure containing both (1,4)- $\alpha$ -D linkages between D-glucose residues and (1,6)- $\alpha$ -D branch points, *Ullmann's Encyclopedia of Industrial Chemistry, Vol. A25, 1994, p. 1-18*. Following formulae depict representative structures of amylose and amylopectin.

15



Representative structure of linear amylose



Representative structure of amylopectin, including (1,6)- $\alpha$ -branch point

Normal starches contain approximately 75% amylopectin molecules the rest consisting of amylose. Amylopectin is a very large molecule with molecular masses ranging from one to several millions. Linearly structured amylose is considerably smaller and the molecular masses usually fall in the range of 5000 –  
5 200000.

Commercial starches are obtained from seeds, particularly corn, wheat, rice, tapioca arrowroot, sago, and potato. Especially in Scandinavia, also barley is utilized as a native starch source. Among these, the starch granules vary in diameter from 1-100  $\mu\text{m}$ . Rice starch has the smallest granules (3-9  $\mu\text{m}$ ), potato  
10 starch ranges between 15-100  $\mu\text{m}$  and corn starch granules are 5-26  $\mu\text{m}$  with an average diameter of 15  $\mu\text{m}$ . Additionally, wheat starch granules are typically from 3 to 35  $\mu\text{m}$  and corresponding barley starch from 5 to 35  $\mu\text{m}$ . *Kirk-Othmer, Encyclopedia of Chemical Technology, 1997, 4th edition, Vol. 22, p. 699-719 and Ketola H, Andersson T, Papermaking Chemistry, 1999, Book 4, p. 269-274.*

15 Due to their extremely high molecular masses as well as chemical composition consisting of both amylose and especially bushlike amylopectin, these branched polysaccharides are practically insoluble into other solvents than water. And in water, the starch granules must be cooked before they will release their water-soluble molecules. In general, they do not form true solutions in water because of  
20 their molecular sizes and intermolecular interactions; rather they form molecular dispersions. Most starch derivatives can be prepared from any native starch but, for reasons of solubility and molecular size, they are mainly produced from potato starch and, in the United States, from waxy maize starch.

Above a certain temperature, characteristic for each type of starch and known as  
25 gelatinization temperature, the starch grains burst and form a gel. The viscosity increases to a maximum, and then decreases asymptotically to a limiting value as the solubilized polymer molecules in water disperse. Complete solubilization of individual molecules of a starch grain only occurs above 100°C, *Ullmann's Encyclopedia of Industrial Chemistry, Vol. A26, 1995, p. 246-248.*

30 The effect of thermal treatment on starches depends strongly on whether it occurs in excess water, limited water, under pressure, or in extrusion cooking. In excess water it appears that starch swelling is a two-stage process consisting of initial granule swelling followed then by granule dissolution. Both of these steps are irreversible. In limited water, thermal responses have been interpreted as being  
35 due to starch crystallite melting. When extrusion cooking is applied, starch

granules are torn physically apart, allowing thus more rapid penetration of water into the granule. In contrast to normal gelatinization, starch fragmentation (dextrinization) appears to be the predominant reaction during extrusion, *Kirk-Othmer, Encyclopedia of Chemical Technology, 1997, 4th edition, Vol. 22, p. 699-719.*

### Organic starch esters

A large number of organic starch esters have been prepared and patented, but only a few are at present manufactured and used commercially. Practically, these are starch acetates (i.e. acetylated starch) and to little extent, starch succinates.

10 Starch acetates may have low or high degree of substitution. The degree of substitution of starch esters is a measure of the average number of hydroxyl groups on each anhydroglucose unit which are derivatized by substituent groups. As each anhydroglucose unit has three hydroxyl groups available for substitution the maximum possible DS is 3. Material with a lower DS (0.3-1.0), i.e. with acetyl  
15 content up to 15%, are soluble in water at 50-100°C. Starch acetates with degrees of substitution of ca. 0.5 have roughly the same solubility as normal starch. Those with high DS (2-3), acetyl content thus exceeding 40%, are soluble in organic solvents with lower polarity (aromatic hydrocarbons, ketones, nitroalkanes etc.) and insoluble in water, diethyl ether, aliphatic alcohols, and aliphatic  
20 hydrocarbons. Starch acetates with such high degree of substitution have increased densities, specific rotations, and melting temperatures. Most of the present commercial products are actually very lightly substituted (DS 0.01-0.2), though.

The industrial importance of low DS acetates results from their ability to stabilize  
25 aqueous polymer solutions. Low DS acetates inhibit association of amylose polymers and reduce the association of the longer outer chains of amylopectin. They also have reduced gelatinization temperature ranges, an increased hot cooked paste viscosity, easier dispersion on cooking as well as reduced tendency to retrograde after pasting and cooling.

30 Retrogradation can be explained as irreversible insolubilization of starch paste with formation of a precipitate or gel depending on concentration and is commonly known as "set back". This is important in food applications but the extremely good viscosity stability gained by acetylation is also strongly wellcomed in applications in paper industry. As a surface size, it improves printability and gives uniform

surface strength, porosity, solvent resistance, and abrasion resistance. Further, low DS starch acetates are employed as warp sizing in textiles to provide good yarn adhesion, tensile strength as well as flexibility.

5 High DS starch acetates are employed in thermoplastic molding as well as in films as plasticizers. Films of such a high DS acetate, cast from chloroform solution, are pliable, lustrous, transparent, and colorless. These properties are useful for instance in packaging materials. Amylose triacetate can also be spun into strong fibers, *Kirk-Othmer, Encyclopedia of Chemical Technology, 1997, 4th edition, Vol.22, p. 699-719* and *Ullmann's Encyclopedia of Industrial Chemistry, Vol. A25,*  
10 **1994, p. 1-18.**

### Acetylation of starch

Literature knows several methods to prepare starch acetates, *Kirk-Othmer, Encyclopedia of Chemical Technology, 1997, 4th edition, Vol. 22, p. 699-719* and *Ullmann's Encyclopedia of Industrial Chemistry, Vol. A25, 1994, p. 1-18.* Most of  
15 the processes typically employ acetic anhydride, with or without catalysts. Commercially, low DS (0,5) acetylated starch is prepared in a system employing acetic anhydride-aqueous alkali at pH 7-11 and room temperature. This method can only be employed when preparing lightly substituted acetylated starches, however. Other methods presented below utilize anhydrous media. In these, the  
20 reaction is very sluggish and, in addition, the granules require time-consuming prior swelling to allow penetration by the acetylation reagents.

Starch granules treated with acetic anhydride alone at 20°C for 5 months does not result in any reaction. At room temperature, pyridine treatment renders the starch granule reactive, though. Treatment with sole acetic anhydride at elevated  
25 temperatures (90-140°C) shows slight activity; cooking and disruption of starch granules increases indeed the reactivity but employing acid catalysts result in starch degradation. When performing the same reaction with acetic anhydride and glacial acetic acid, the reaction requires the addition of an acidic catalyst such as sulfuric acid, perchloric acid or phosphoric acid.

30 Treatment of starch with acid anhydride in DMSO (dimethyl sulfoxide) requires expensive triethylamine as a catalyst and acid scavenger. With this method, starch derivatives of acetic, propanoic, and butanoic anhydrides have been prepared up to DS of 0.08.

When employing glacial acetic acid alone at 100°C for 5-13 h, the esterification gives a product with 3-6% content of acetyl groups. Treatment of starch with concentrated formic acid leads to gelatinization and simultaneous esterification.

- 5 Acetylation with ketene produces starch with an acetyl content of 2.2-9.4%. The reaction is usually conducted in acetic acid, diethyl ether or acetone with an acid catalyst.

- 10 Also vinyl acetate has been employed in the acetylation. Thus, for example US 3 022 289 discloses a method of chemically modifying starch comprising reacting starch in the presence of an alkaline catalyst, such as an alkali metal carbonate or hydroxide, ammonium hydroxide or an aliphatic amine, and more than 10% water by weight of dry starch with an ester of a carboxylic acid and an ethylenically unsaturated alcohol, such as vinyl acetate.

Preparation of high DS starch acetates always requires the use of anhydrous methods described previously, but also prolonged reaction times.

- 15 US 2 461 139 discloses a method for preparing starch esters. The method includes reacting starch and water with an organic acid anhydride and maintaining the pH of the reaction in the alkaline range between 7 and 11. The organic acid anhydrides include acetic anhydride, propionic anhydride, phthalic anhydride and butyric anhydride. Typically, starch is suspended in water at 25°-30°C and sodium  
20 hydroxide is added to raise the pH to about 10. Then enough acetic anhydride is added to the suspension to lower the pH to about 7 followed by separating the starch ester by filtration.

- 25 GB 1 425 624 discloses a process for the chemical modification of starch. The method includes the step of subjecting a mixture of starch and a modifying agent to microwave energy under such conditions that the water content during the radiation treatment is or reduces to less than 10% by weight of the starch. The application of microwaves is said to reduce the reaction time and increase the yields. According to GB 1 425 624 the chemical modifications include dextrination, oxidation, hydrolysis and derivatisation with monofunctional or polyfunctional  
30 etherifying and esterifying agents. Typically, the starch is suspended in an aqueous solution or suspension of the modifying agent. After stirring the suspension is dried and the obtained starch reaction mixture is subjected to microwave radiation in a fluidised bed. Due to the low water content and the absence of any liquid medium the modification is carried out in solid phase.

## Ionic liquids

The literature knows many synonyms used for ionic liquids. Up to date, "molten salts" is maybe the most broadly applied term for ionic compounds in the liquid state. There is a difference between molten salts and ionic liquids, however. Ionic liquids are salts that are liquid around room temperature (typically -100°C to 200°C, but this might even exceed 300°C) (Wassercheid, P.; Welton, T. *Ionic Liquids in Synthesis* 2003, WILEY-VCH, p. 1-6, 41-55 and 68-81). Therefore, the term RTIL (room temperature ionic liquids) is commonly applied for these solvents.

RTILs are non-flammable, non-volatile and they possess high thermal stabilities. Typically, these solvents are organic salts or mixtures consisting of at least one organic component. By changing the nature of the ions present in an RTIL, it is possible to change the resulting properties of the RTILs. The lipophilicity of an ionic liquid of a RTIL is easily modified by the degree of cation substitution. Similarly, the miscibility with for example water and other protic solvents can be tuned from complete miscibility to almost total immiscibility, by changing the anion substitution.

All these variations in cations and anions can produce a very large range of ionic liquids allowing the fine-tuning for specific applications. Furthermore, the RTILs are relatively cheap and easy to manufacture. They can also be reused after regeneration.

US 1 943 176 discloses a process for the preparation of solutions of cellulose by dissolving cellulose under heating in a liquefied N-alkylpyridinium or N-benzylpyridinium chloride salt, preferably in the presence of an anhydrous nitrogen-containing base, such as pyridine. These salts are known as ionic liquids. The cellulose to be dissolved is preferably in the form of regenerated cellulose or bleached cellulose or linter. According to US 1 943 176 the cellulose solutions are suitable for various chemical reactions, such as esterification. US 1 943 176 also suggests separating cellulose from the cellulose solution by means of suitable precipitating agents, such as water or alcohol to produce for example cellulose threads or films or masses.

Also WO 03/029329 suggests dissolving pure cellulose in various ionic liquids especially under microwave irradiation. The dissolved cellulose can be regenerated in a range of structural forms.

## Microwaves

- It is known from the recent literature concerning organic synthesis that the reaction times of the organic reactions are remarkable reduced when the energy necessary for the occurrence of the reaction is introduced to the system by using microwave irradiation. The commonly used frequency for microwave energy is 2.45 GHz. There is a wide and continuously increasing literature available in the area of using microwave techniques in organic synthesis. An example of a short summary article of this topic was published by Mingos in 1994 (D. Michael P. Mingos; "Microwaves in chemical synthesis" in *Chemistry and industry* 1. August 1994, pp. 596-599).
- Loupy *et. al.* have recently published a review concerning heterogenous catalysis under microwave irradiation (Loupy, A., Petit, A., Hamelin, J., Texier-Boullet, F., Jachault, P., Mathe, D.; "New solvent-free organic synthesis using focused microwave" in *Synthesis* 1998, pp. 1213-1234). Another representative article of the area is published by Strauss as an invited review article (C.R. Strauss; "A combinatorial approach to the development of Environmentally Benign Organic Chemical Preparations", *Aust. J. Chem.* 1999, 52, 83-96).

## Summary of the invention

- It is an object of this invention to provide a method for preparing organic starch esters.
- The present invention is based on the surprising discovery that native starch as well as hydrolyzed starch can be dissolved in an ionic liquid, the dissolved starch can be acetylated with acetic anhydride without any catalysts, and the acetylated starch ester can be precipitated from the reaction medium by the addition of various alcohols.
- Thus, this invention accomplishes an efficient, gentle and environmentally benign preparation of organic starch esters in ionic liquids and a simple, economical separation of reaction products by precipitating the prepared product by adding a non-solvent for the product.

## Brief description of the drawings

- In the enclosed drawings Fig. 1 shows a spectrum obtained by FTIR analysis of a acetylated starch sample prepared by the method of the present invention, Fig 2 shows a spectrum obtained by FTIR analysis of a propionylated starch sample prepared by the method of the present invention, and Fig. 3 shows a spectrum

obtained by FTIR analysis of a starch maleic ester sample prepared by the method of the present invention.

### Detailed description of the invention

5 According to the invention there is provided a method for preparing an organic starch ester, said method comprising mixing a starch material with an ionic liquid solvent to dissolve the starch, and then treating the dissolved starch with an organic esterifying agent to form an organic starch ester, and subsequently separating the organic starch ester from the solution.

10 The starch material can be any untreated or treated starch material, such as native starch or hydrolyzed starch. The starch can be derived from e.g. corn, wheat, rice, tapioca arrowroot, sago, potato or barley.

The dissolution and esterification can be assisted by applying microwave irradiation and/or pressure.

15 The pressure is preferably at most 2.0 MPa and more preferably between 1.5 MPa and 2.0 MPa.

20 The dissolution of the starch material can be carried out at a temperature between 0°C and 250°C, preferably at a temperature between 10°C and 170°C, such as between 20°C and 130°C. If microwave irradiation is applied, the heating can be carried out by means of this irradiation. The solution is agitated until complete dissolution is obtained.

In the dissolution no auxiliary organic solvents or co-solvents, such as nitrogen-containing bases, e.g. pyridine, are necessary. Preferably such solvents are omitted.

25 The dissolution is preferably carried out in the substantial absence of water. The phrase "in the substantial absence of water" means that not more than a few percent by weight of water is present. Preferably, the water content is less than 1 percent by weight.

The starch can be present in the solution in an amount of about 1% to 35% by weight of the solution. Preferably the amount is from about 10% to about 20%.

30 The esterification can be carried out at the same temperature as the dissolution or at a lower temperature. The esterification is preferably also carried out in the

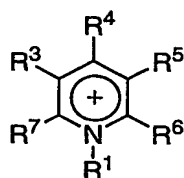


substantial absence of water. No catalysts are necessary, and the esterification is preferably carried out without a catalyst.

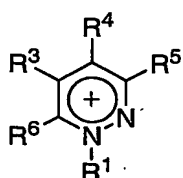
The ionic liquid solvent is molten at a temperature between -100°C and 200°C, preferably at a temperature of below 170°C, and more preferably between -50°C and 120°C.

The cation of the liquid solvent is preferably a five- or six-membered heterocyclic ring optionally being fused with a benzene ring and comprising as heteroatoms one or more nitrogen, oxygen or sulfur atoms. The heterocyclic ring can be aromatic or saturated. The cation can be selected from the group consisting of

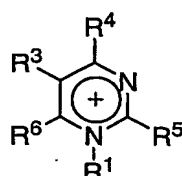
10



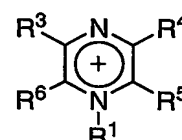
Pyridinium



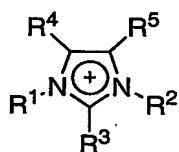
Pyridazinium



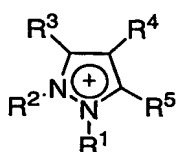
Pyrimidinium



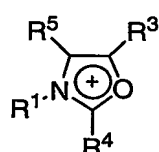
Pyrazinium



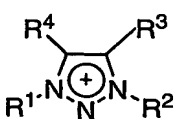
Imidazolium



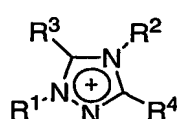
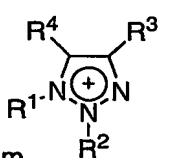
Pyrazolium



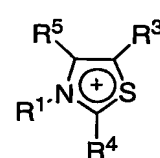
Oxazolium



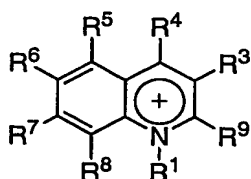
1,2,3-Triazolium



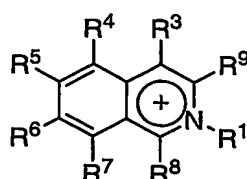
1,2,4-Triazolium



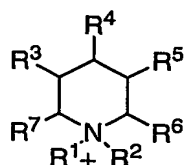
Thiazolium



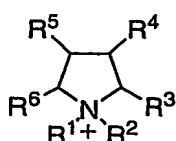
Quinolinium



Isoquinolinium



Piperidinium



Pyrrolidinium

wherein  $R^1$  and  $R^2$  are independently a  $C_1$ - $C_6$  alkyl or  $C_2$ - $C_6$  alkoxyalkyl group, and  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$  and  $R^9$  are independently hydrogen, a  $C_1$ - $C_6$  alkyl,  $C_2$ - $C_6$  alkoxyalkyl or  $C_1$ - $C_6$  alkoxy group.

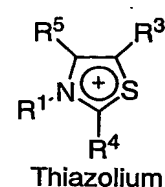
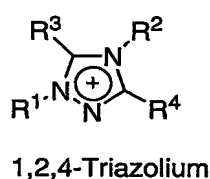
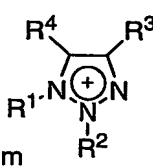
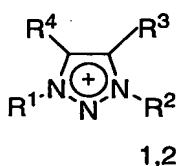
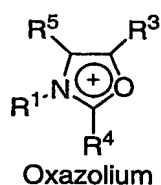
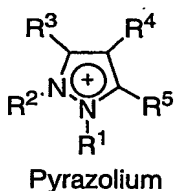
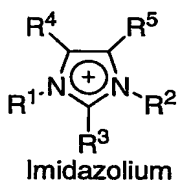
In the above formulae  $R^1$  and  $R^2$  are preferably both  $C_1$ - $C_4$  alkyl, and  $R^3$ - $R^9$ , when present, are preferably hydrogen.

$C_1$ - $C_6$  alkyl includes methyl, ethyl, propyl, iso-propyl, butyl, sec-butyl, tert-butyl, pentyl, the isomers of pentyl, hexyl and the isomers of hexyl.

$C_1$ - $C_6$  alkoxy contains the above  $C_1$ - $C_6$  alkyl bonded to an oxygen atom.

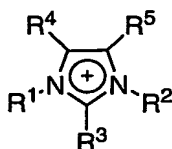
$C_2$ - $C_6$  alkoxyalkyl is an alkyl group substituted by an alkoxy group, the total number of carbon atoms being from two to six.

Preferred cations have following formulae:



wherein  $R^1$ - $R^5$  are as defined above.

An especially preferred cation is the imidazolium cation having the formula:



wherein  $R^1$ - $R^5$  are as defined above. In this formula  $R^3$ - $R^5$  are preferably each hydrogen and  $R^1$  and  $R^2$  are independently  $C_1$ - $C_6$  alkyl or  $C_2$ - $C_6$  alkoxyalkyl. More preferably one of  $R^1$  and  $R^2$  is methyl and the other is  $C_1$ - $C_6$  alkyl.

The anion of the ionic liquid solvent can be halogen such as chloride, bromide or iodide;

pseudohalogen such as thiocyanate or cyanate;

perchlorate;

- 5 C<sub>1</sub>-C<sub>6</sub> carboxylate such as formate, acetate, propionate, butyrate, lactate, pyruvate, maleate, fumarate or oxalate;

nitrate;

C<sub>2</sub>-C<sub>6</sub> carboxylate substituted by one or more halogen atoms such as trifluoroacetic acid;

- 10 C<sub>1</sub>-C<sub>6</sub> alkyl sulfonate substituted by one or more halogen atoms such as trifluoromethane sulfonate (triflate);

tetrafluoroborate BF<sub>4</sub><sup>-</sup>, or

phosphorus hexafluoride PF<sub>6</sub><sup>-</sup>.

The above halogen substituents are preferably fluoro.

- 15 The anion of the ionic liquid solvent is preferably selected among those providing a hydrophilic ionic liquid solvent. Such anions include halogen, pseudohalogen or C<sub>1</sub>-C<sub>6</sub> carboxylate. The halogen is preferably chloride, bromide or iodide, and the pseudohalogen is preferably thiocyanate or cyanate.

- 20 If the cation is a 1-(C<sub>1</sub>-C<sub>6</sub>-alkyl)-3-methyl-imidazolium, the anion is preferably a halogen, especially chloride.

A preferred ionic liquid solvent is 1-butyl-3-methyl-imidazolium chloride (BMIMCl) having a melting point of about 60°C.

- 25 The organic esterifying agent is preferably a C<sub>1</sub>-C<sub>11</sub>, more preferably a C<sub>1</sub>-C<sub>6</sub> carboxylic acid or a reactive derivative thereof. The hydrocarbon moiety of the organic esterifying agent can be saturated or unsaturated, aliphatic or aromatic, and may optionally be substituted by one or more of following groups: carboxylic, halide, amino, hydroxyl ether and epoxy. Typical esterifying agents include formic acid, acetic acid, propanoic acid, butanoic acid, maleic acid, malic acid, succinic acid, itaconic acid, chloroacetic acid, alanine and phthalic acid, and corresponding

anhydrides. It is also possible to use other reactive derivatives of carboxylic acids, such as halogens or esters formed with ethylenically unsaturated alcohols, such as vinyl esters.

5 The organic starch ester prepared by the method of the present invention can have a degree of substitution of 1 to 3. The hydrocarbon moiety of the organic ester group can be saturated or unsaturated, aliphatic or aromatic, and may optionally be substituted by one or more of following groups: carboxylic, halide, amino, hydroxyether, and epoxy. The hydrocarbon moiety preferably comprises from 1 to 10 carbon atoms. Typical esters include acetic, propanoic, butanoic,  
10 maleic, malic, succinic, itaconic, chloroacetic, alanine and phthalic esters.

After the esterification the obtained organic starch ester can be separated from the solution by adding a non-solvent for the organic starch ester to precipitate the organic starch ester. The non-solvent should also be a non-solvent for the ionic liquid solvent and miscible with the ionic liquid solvent. Said non-solvent is  
15 preferably an alcohol, such as a C<sub>1</sub>-C<sub>6</sub> alkanol, for example methanol, ethanol, propanol or isopropanol. Also other non-solvents, such as ketones (e.g. acetone), acetonitrile, polyglycols and ethers can be used. With appropriate DS of the organic starch esters, even water can be employed as a non-solvent.

It is also possible to separate the obtained organic starch ester by extraction with a  
20 suitable solvent that is a non-solvent for the ionic liquid solvent.

In a preferred embodiment of the invention, the method comprises the steps of:

- (a) admixing native or hydrolyzed starch with an ionic liquid solvent in the substantial absence of water to form an admixture,
- (b) stirring the admixture until the dissolution is complete,
- 25 (c) reacting the dissolved starch in the ionic liquid solvent with an organic esterifying agent in the absence of a catalyst for preparing an organic starch ester, and
- (d) precipitating the organic starch ester from the reaction mixture by adding a non-solvent for the organic starch ester.

30 The main advantages of preferred methods of the present invention for the preparation of organic starch esters in ionic liquids are as follows:

- complete and fast dissolution of starch at temperatures below 100°C
- due to good solubility, possibility to employ all native starches in organic starch ester preparation
- reactions in non-aqueous media, which in turn accomplishes fast and economical separation of reaction products by precipitating the prepared product by adding a non-solvent for the product, and further, a simple, energy efficient drying procedure of the products
- possibility to separate the products with extraction with a non-solvent for the ionic liquid
- fast preparation of organic starch esters
- dramatically shorter reaction times and lower reaction temperatures by use of microwave irradiation and/or pressure
- easy control of the degree of substitution (DS)
- efficient preparation also of highly substituted organic starch esters
- preparation of organic starch esters without acid catalysts
- gentle reaction conditions diminishing the risk of chain degradation
- environmentally benign technique without use of harmful solvents as the ionic liquids can be reused.

The percentages in this specification refer to % by weight unless otherwise specified.

## Examples

### Example 1

#### *Acetylation of native barley starch*

A 150 mg (1 mmol) sample of oven dried native barley starch was added into ionic liquid (BMIMCl, 3 ml) and the resulting mixture was stirred at 75°C for 25 minutes. A clear, 5% starch solution was formed and acetic anhydride (0.3 ml, 3 mmol) was added therein. The reaction was conducted for 15 minutes and quenched by adding dry ethanol (3 ml) with a syringe into the reaction mixture. While stirring the resulting mixture, the product precipitated from the reaction medium. The product was filtered off and washed with dry ethanol, oven dried and analyzed with FTIR. The obtained spectrum for acetylated starch is shown in Fig. 1 showing the acetyl OAc peak at 1737.1 cm<sup>-1</sup>.

**Example 2***Acetylation of hydrolyzed starch*

A 150 mg (1 mmol) sample of oven dried, hydrolyzed starch was added into ionic liquid (BMIMCl, 3 ml) and the resulting mixture was stirred at 75°C for 25 minutes.

5 A clear, 5% starch solution was formed and acetic anhydride (0.3 ml, 3 mmol) was added therein. The reaction was conducted for 15 minutes and quenched by adding dry isopropanol (3 ml) with a syringe into the reaction mixture. While stirring the resulting mixture, the product precipitated from the reaction medium. The product was filtered off and washed with dry isopropanol, oven dried and

10 analyzed with FTIR. The spectrum was in accordance with the one shown in Fig. 1.

**Example 3***Propionylation of native barley starch, D.S. = 1*

A 2 g (12.4 mmol) sample of oven dried native barley starch was added into ionic liquid (BMIMCl, 20 g) and the resulting mixture was stirred at 80°C for 20 minutes.

15 A faintly opaque, 10% starch solution was formed and propionic anhydride (1.6 ml, 12.4 mmol) was slowly added therein. The reaction was conducted for 2 hours and quenched by adding ethanol (30 ml) into the reaction mixture. While stirring the resulting mixture, the product precipitated from the reaction medium. The product

20 was filtered off and washed with ethanol, oven dried and analyzed with FTIR. The obtained spectrum for propionylated starch is shown in Fig. 2 showing the O-propionyl peak at  $1736.9\text{ cm}^{-1}$ . The prepared propionylated starch was soluble in water, but insoluble in alcohols such as methanol, ethanol and isopropanol.

**Example 4**

25 *Propionylation of native barley starch, D.S. = 2*

A 2 g (12.4 mmol) sample of oven dried native barley starch was added into ionic liquid (BMIMCl, 20 g) and the resulting mixture was stirred at 80°C for 20 minutes. A faintly opaque, 10% starch solution was formed and propionic anhydride (3.2 ml, 24.7 mmol) was slowly added therein. The reaction was conducted for 2 hours and

30 quenched by adding ethanol (35 ml) into the reaction mixture. While stirring the resulting mixture, the product precipitated from the reaction medium. The product was filtered off and washed with ethanol, oven dried and analyzed with FTIR. The

spectrum was in accordance with the one shown in Fig. 2. The prepared propionylated starch was somewhat soluble in water, and the precipitation with alcohols such as ethanol and methanol was not as unconditioned as with propionylated starch product in example 3.

## 5 Example 5

### *Propionylation of native barley starch, D.S. = 3*

A 2 g (12.4 mmol) sample of oven dried native barley starch was added into ionic liquid (BMIMCl, 20 g) and the resulting mixture was stirred at 80°C for 20 minutes. A faintly opaque, 10% starch solution was formed and propionic anhydride (4.8 ml, 37.1 mmol) was slowly added therein. The reaction was conducted for 3 hours and quenched by adding water (30 ml) into the reaction mixture. While stirring the resulting mixture, the product precipitated from the reaction medium. The product was filtered off and washed with water, oven dried and analyzed with FTIR. The spectrum was in accordance with the one shown in Fig. 2. The prepared propionylated starch was insoluble in water, faintly soluble in methanol and even more, in ethanol.

## Example 6

### *Esterification of native barley starch with maleic anhydride, D.S. = 1*

A 1 g (6.2 mmol) sample of oven dried native barley starch was added into ionic liquid (BMIMCl, 10 g) and the resulting mixture was stirred at 80°C for 20 minutes. A faintly opaque, 10% starch solution was formed and maleic anhydride (606 mg, 6.2 mmol) was slowly added therein. The reaction was conducted for 2 hours and quenched by adding methanol (30 ml) into the reaction mixture. While stirring the resulting mixture, the product precipitated from the reaction medium. The product was filtered off and washed with methanol, oven dried and analyzed with FTIR. The obtained spectrum for starch maleic ester is shown in Fig. 3 showing the maleic ester peak at 1726.0 cm<sup>-1</sup> and carboxylic acid giving its characteristic peaks at 1642.1 cm<sup>-1</sup> and 1415.6 cm<sup>-1</sup>. The prepared starch maleic ester was soluble in water, but insoluble in alcohols such as methanol, ethanol and isopropanol. The product is hygroscopic.

**Example 7***Esterification of native barley starch with maleic anhydride, D.S. = 2*

A 1 g (6.2 mmol) sample of oven dried native barley starch was added into ionic liquid (BMIMCl, 10 g) and the resulting mixture was stirred at 80°C for 20 minutes. A clear, 10% starch solution was formed and maleic anhydride (1212 mg, 12.4 mmol) was slowly added therein. The reaction was conducted for 2 hours and quenched by adding a solution of methanol and isopropanol (1:1, 40 ml) into the reaction mixture. While stirring the resulting mixture, the product precipitated from the reaction medium. The product was filtered off and washed with a solution of methanol and isopropanol (1:1), oven dried and analyzed with FTIR. The spectrum was in accordance with the one shown in Fig. 3. The prepared starch maleic ester was soluble in water, but insoluble in alcohols such as methanol and isopropanol. The product is hygroscopic.

**Example 8***Esterification of native barley starch with maleic anhydride, D.S. = 3*

A 1g (6.2 mmol) sample of oven dried native barley starch was added into ionic liquid (BMIMCl, 10 g) and the resulting mixture was stirred at 80°C for 20 minutes. A clear, 10% starch solution was formed and maleic anhydride (1818 mg, 18.6 mmol) was slowly added therein. The reaction was conducted for 3 hours and quenched by adding a solution of methanol and isopropanol (1:1, 40 ml) into the reaction mixture. While stirring the resulting mixture, the product precipitated from the reaction medium. The product was filtered off and washed with a solution of methanol and isopropanol (1:1), oven dried and analyzed with FTIR. The spectrum was in accordance with the one shown in Fig. 3. The prepared starch maleic ester was soluble in water, but insoluble in alcohols such as methanol and isopropanol. The product is hygroscopic.